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明 細 書

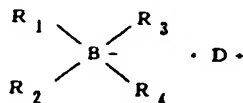
1. 発明の名称

近赤外光硬化型インキ

2. 特許請求の範囲

一般式(1)で表される近赤外光重合開始剤を含むことを特徴とする近赤外光硬化型インキ

一般式(1)



(式中、D・は近赤外領域に吸収をもつ陽イオン色素であり、R₁、R₂、R₃及びR₄は各々独立にアルキル、アリール、アルカリール、アリル、アラルキル、アルケニル、アルキニル、脂環式及び飽和または不飽和複素環式基を示し、R₁、R₂、R₃及びR₄の中の少なくとも1個は炭素原子数1～8個のアルキル基である。)

3. 発明の詳細な説明

(1) 産業上の利用分野

本発明は、印刷インキに好適に使用し得る近赤外光硬化型インキに関する。

(2) 従来の技術

近年、印刷インキの無溶剤化による公害防止、急速硬化による生産性の向上、あるいは、硬化皮膜の物性改良を目的として紫外光硬化型インキの開発が盛んに進められている(例えば、特開平1-229084、特開平1-271469及び特開平2-22370)。特開平2-22370明細書には、ポリ(メタ)アクリル酸エステルと紫外光重合開始剤を含むことを特徴とし、硬化速度及び皮膜硬度の優れた紫外光硬化型インキについて開示されている。

(3) 発明が解決しようとする課題

紫外光硬化インキは、200～400nmの紫外光を照射することによってカチオン重合あるいはラジカル重合によって重合性モノマーが急速硬化するものである。紫外光硬化インキの基本的な組成は色材、光活性ビヒクル、光重合開始剤及び助剤からなり、このうち色材については一般に使用される顔料、染料が用いられる。また、活性ビヒクル

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クリレート、ビスフェノールAテトラエチレングリコールジアクリレート、ビスフェノールAテトラエチレングリコールジメタクリレート、ビスフェノールFポリエチレングリコールジアクリレート、ビスフェノールFポリエチレングリコールジメタクリレート、トリシクロデカンジメチロールジアクリレート、トリシクロデカンジメチロールジメタクリレート、トリメチロールプロパントリプロポキシトリアクリレート、トリメチロールプロパントリプロポキシトリメタクリレート、ジトリメチロールプロパンテトラアクリレート、ジトリメチロールプロパンテトラメタクリレート、トリメチロールプロパンポリエトキシトリアクリレート、トリメチロールプロパンポリエトキシトリメタクリレート、ヒドロキシビバリン酸ネオペンチルグリコールジアクリレート、ヒドロキシビバリン酸ネオペンチルグリコールジメタクリレート、ジペンタエリスリトールペンタ（またはヘキサ）アクリレートまたはメタクリレート等、トリペンタエリスリトール、テトラペンタエ

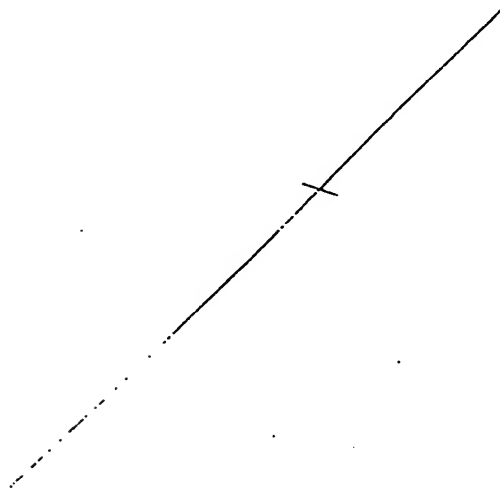
リスリトールのアクリル酸エステル及びメタクリル酸エステル等のエチレン性不飽和モノマー類が挙げられる。

なかでも、好適な例としてはエポキシ化大豆油、エポキシ化ロジン等のエポキシアクリレート類及びウレタン変性物、脂肪酸変性アルキッド樹脂のアクリル酸エステル、ウレタンアクリレート、ウレタンメタクリレート、エポキシアクリレート、エポキシメタクリレート、ビスフェノールAテトラエチレングリコールジアクリレート、トリメチロールプロパントリプロポキシトリアクリレート、トリペンタエリスリトール、テトラペンタエリスリトールのアクリル酸エステル及びメタクリル酸エステル等を挙げることができる。

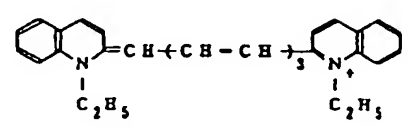
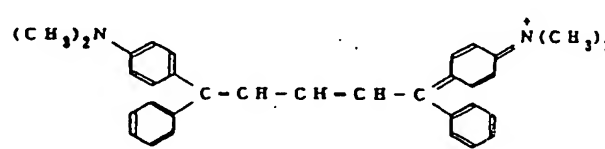
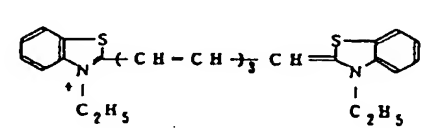
本発明に用いられる近赤外光重合開始剤としては、一般式(1)で表される陽イオン性染料・ボレート錯体であり、これを構成する陽イオン染料の特定な種類は近赤外領域に吸収をもつシアニン、トリアリールメタン、アミニウム、ジインモニウム系色素であり、ボレート陰イオンの R_1 、 R_2 、

R_3 及び R_4 は各々独立にアルキル、アリール、アルカリール、アリル、アラルキル、アルケニル、アルキニル、脂環式及び飽和または不飽和複素環式基を示し、 R_1 、 R_2 、 R_3 及び R_4 の中の少なくとも1個は炭素原子数1～8個のアルキル基である。

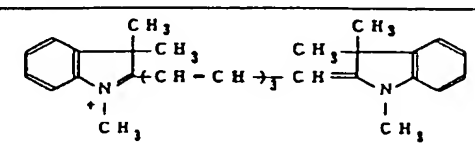
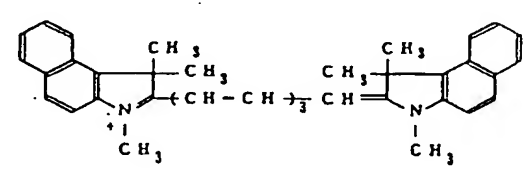
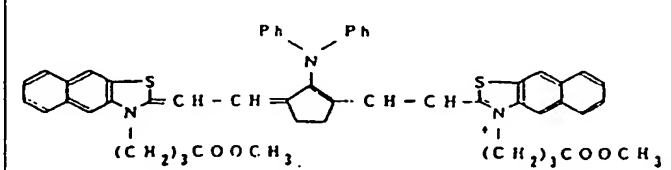
本発明に特に有用な開始剤の例を第1表に示す。

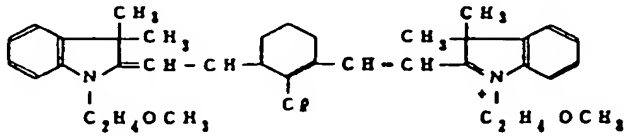
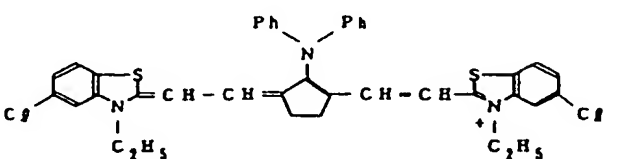
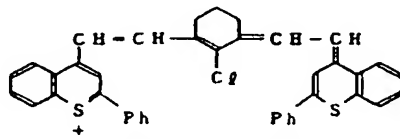


第 1 表

開始剤番号	構造	R	Ar	λ (TMPA)
1	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			820nm
2	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			830nm
3	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			768nm

第 1 表 (続 き)

開始剤番号	構造	R	Ar	λ (TMPA)
-A 4-B -C	 $\text{Ar}_3\text{B}^- \cdot \text{R}$	n-ブチル n-ヘキシル n-オクチル	フェニル アニシル フェニル	748nm 748nm 748nm
-A 5-B -C	 $\text{Ar}_3\text{B}^- \cdot \text{R}$	n-ブチル n-ヘキシル n-オクチル	フェニル アニシル フェニル	758nm 758nm 758nm
-A 6-B -C	 $\text{Ar}_3\text{B}^- \cdot \text{R}$	n-ブチル n-ヘキシル n-オクチル	フェニル アニシル フェニル	828nm 828nm 828nm

開始剤番号	構 造	R	Ar	λ (TMPA)
7	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			787nm
8	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			819nm
9	 $\text{Ph}_3\text{B}^- \cdot n\text{-C}_4\text{H}_9$			1080nm

λ は吸収波長を表す。 Ph は、フェニル基を表す。 TMPAは、トリメチロールプロパントリメタクリレートを表す。

本発明の近赤外光硬化型インキは、前記のエチレン性不飽和基を含有するモノマー及びプレポリマーに近赤外光重合開始剤を好ましくは、0.01～10重量%、特に0.1～5重量%の割合で混合して形成したものが好ましい。本発明の近赤外光硬化型インキには、さらに必要によって固形の非反応性樹脂、例えば、ジアリルフタレート樹脂、環状ケトン樹脂、天然樹脂変性フェノール樹脂、アクリル樹脂等を加えて、硬化皮膜等を改良することができるが、その配合量は、本発明の近赤外光硬化型インキに対して30%以下が適当である。

本発明の近赤外光硬化型インキには、着色顔料の外、必要に応じて重合禁止剤、可塑剤、充填剤、溶剤並びに酸基除去剤及び連鎖移動剤等の助剤類を併用することができる。

本発明の近赤外光硬化型インキは、紫外光硬化型インキが使用されている枚葉平板印刷、金属板印刷、オフ輪印刷、ビジネスフォーム印刷、ラベルシート印刷、曲面印刷、凸オフ印刷、タンポ印刷、スクリーン印刷などの印刷インキとして有用

であるが、その他に、紙のつや出しコーティング剤、保護コーティング、ソルダーレジスト等としても有用である。

本発明の近赤外光硬化型インキは、紙、プラスチック及び金属などに印刷された後、半導体レーザー、ハロゲンランプ及び発光ダイオードなどにより近赤外光を照射し硬化させ、強度の優れた印刷皮膜を得ることができる。

印刷インキへの適用の具体的な例としては、枚葉平板印刷インキとして使用でき、化粧品、食品パッケージに用いられるアルミ фоль紙に、この近赤外光硬化型インキにて5 μm の厚さで印刷し、近赤外光照射装置で照射することによって、浸透乾燥性のないアルミ фоль紙へ乾燥定着を行うことができる。

以下、実施例をあげて本発明をさらに説明する。

実施例 1

ベニグエリスチートールメタクリレート40重量部、
 (新日村化学社製、
 U...A...製品部...アルテト

ラエチレングリコールジトリアクリレート5重量部、Rubine GL - SE (日本化薬社製) 19重量部及び近赤外光重合開始剤 (開始剤番号1) 1重量部を3本ロールで練肉して近赤外光硬化型インキAを得た。

実施例 2

ペンタエリスリトールテトラアクリレート40重量部、エポキシアクリレート (日本化薬社製、カラヤッドR-167) 30重量部、トリメチロールプロパントリプロポキシトリアクリレート10重量部、Rubine GL - SE (日本化薬社製) 19重量部及び近赤外光重合開始剤 (開始剤番号1) 1重量部を3本ロールで練肉して近赤外光硬化型インキBを得た。

実施例 3

ペンタエリスリトールトリアクリレート40重量部、ウレタンアクリレート (新中村化学社製、U-108-A) 35重量部、ビスフェノールAテトラエチレングリコールジトリアクリレート5重量部、Navy Blue 2G - SF 200 (日本化薬社製)

19重量部及び近赤外光重合開始剤 (開始剤番号4A) 2重量部を3本ロールで練肉して近赤外光硬化型インキCを得た。

実施例 4

ジペンタエリスリトールペンタアクリレート40重量部、エポキシアクリレート (日本化薬社製、カラヤッドR-167) 30重量部、ビスフェノールAテトラエチレングリコールジトリアクリレート10重量部、Navy Blue 2G - SF 200 (日本化薬社製) 19重量部及び近赤外光重合開始剤 (開始剤番号6A) 0.5重量部を3本ロールで練肉して近赤外光硬化型インキDを得た。

比較例 1

実施例1で、近赤外光重合開始剤 (開始剤番号1) をo-ベンゾイル安息香酸メチル10重量部に変える以外は実施例1と同様にして近赤外光硬化型インキEを得た。

インキ性能評価方法

硬化時間：実施例1～4及びインキ0.6gをRIテスターを用いてカルトン紙に展色し、ただ

ちにアルミニウムコート型ハロゲンランプ (2W/cd) で照射した後、RIテスターによりアート紙に圧着し、インキが付着しなくなるまで要した照射時間 (秒) を硬化時間とした。

皮膜硬度：硬質塩ビ板にバーコーターにより膜厚10ミクロンになるように塗布し、アルミニウムコート型ハロゲンランプ (2W/cd) で1秒間照射し硬化させた。ついで、JIS-K-5400に基づいて、鉛筆硬度を測定した。

硬化時間及び鉛筆硬度の測定結果を第2表に示す。

第 2 表

インキ	硬化時間 (秒)	鉛筆硬度
A	0.5	5H
B	0.5	5H
C	0.3	5H
D	0.7	5H
E	未硬化	-

(6) 発明の効果

本発明により、近赤外光で硬化し、硬化速度が速くかつ皮膜硬度が大きい近赤外光硬化型インキが提供される。

特許出願人 昭和電工株式会社

代 理 人 弁 理 士 寺 田 貢

HOR-010

TECHNOLOGY CENTER 1700
COVER SHEET

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TO: Mr. Bruce Monroe

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PHONE NUMBER: 302-479-9470

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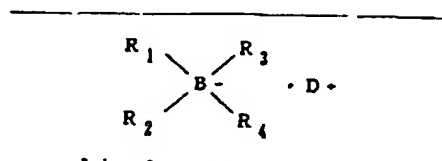
Japanese Published Unexamined (Kokai) Patent Application No. H4-39367, published February 10, 1992; Application No. H2-146741, filed June 4, 1990; Int. CL⁵: C09D 11/00 11/02 11/10; Inventor(s): Katsumi Murofuse et al.; Assignee: Showa Denko Corporation; Japanese Title: Kinsekigaikou Koukagata Inki (Near Infrared Photocuring Ink)

1. Title of Invention

Near Infrared Photocuring Ink

2. Claim

A near infrared Photocuring ink, characterized in that a near infrared photopolymerization initiator which is indicated by a general formula (1) is contained:



(In the formula, D⁺ stands for a positive ion pigment that has an absorption in a near infrared area; R₁, R₂, R₃ and R₄ separately stand for an alkyl group, an aryl group, an alkyl group, an allyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alicyclic group and a saturated or unsaturated heterocyclic group; at least one of said Rs is said alkyl group of 1 to 8 carbon atoms.)

3. Detailed Description of the Invention

(1) Field of Industrial Application

This invention pertains to near infrared photocuring inks that can be suitably used for

printing inks.

(2) Prior Art

In the recent years, for the purposes of the prevention of a pollution due to a nonuse of solvents for printing inks, an improved productivity by a quick curing or an improved properties of cured films, ultraviolet photocuring inks have been increasingly developed (for example, the following patent applications indicates said development: Japanese unexamined patent application No. H1-229084; Japanese unexamined patent application No. H2-22370). The specification of application No. H2-22370 mentions about an ultraviolet photocuring ink with an excellent curing speed and an excellent film curing, characterized by containing poly (metha) acrylic ester and an ultraviolet photopolymerization initiator.

(3) Problem of Prior Art to Be Addressed

Ultraviolet photocuring inks work such that, by radiating a 200 to 400 nm ultraviolet ray, a polymerizing monomer quickly cures due to a cationic polymerization and a radical polymerization. Said ultraviolet photocuring inks are basically composed of the following components: coloring materials; photoactivated vehicles; photopolymerization initiators; aides; conventional pigments and dyes are used as coloring materials. The following substances are practically the main components of said photoactivated vehicles: ester acrylate and monomers and polymers which are the derivatives thereof. The following substances are used as photopolymerization initiators: acetophenone derivatives; benzoin derivatives; hydrogen extracting initiators that are composed of benzophenone derivatives and amines as hydrogen

donors; directly photolyzing initiators such as benzoin alkyl ether and the like.

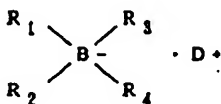
In the printing industry, said inks are printed so as to form thin films at 1 to 3 μm ; said films are cured by radiating ultraviolet rays by a drying means. Since said ultraviolet photocuring inks are curable at a high speed, they are used for the following printing means: sheet-fed lithography that prints polyester sheets used for cosmetics and food packages; a label-sheet printing that prints label sheets such as aluminum foil sheets, polyester, mirror coat applied sheets and art coat applied sheets; a curved-surface printing that prints containers made of styrol, foamed styrol, polystyrene or polypropylene; an off-letterpress printing that prints panels; a *tanpo* (a type of printing means) printing that prints the dials of clocks and electronic parts; a screen printing that prints plastic containers and printed boards. Since said ultraviolet photocuring inks also have an energy saving property and a high strength of ink applied films, they can be also used for the following types of printing means: a metal plate printing that prints food and drink cans; an off-rotary printing that is used for printing text books; a business-form printing that prints documents and journals. However, as for said ultraviolet photocuring inks used for said purposes as described above, the photopolymerization initiator demonstrates a sensitivity on a 200 to 400 nm ultraviolet ray; because said ultraviolet rays basically have a low transmittance in relation to monomers, ultraviolet photocuring inks are not preferred when opaque paints or thick films are used; when the film thickness increases, the surface alone is cured or the curing period increases.

The present invention aims to offer a near infrared photocuring ink with a high curing speed and an excellent printed film hardness by using a near infrared light with an excellent transmittance.

(4) Measures to Solve the Problem

After the inventor of the present invention have eagerly researched, by using a near infrared photopolymerization initiator as a photopolymerization initiator, which is indicated by general formula (1) as indicated below, with a monomer and a prepolymer that contain ethylene unsaturated groups generally used as activated vehicles, the ink is cured with a near infrared light; by means of this, a near infrared photocuring ink with a high curing speed and an excellent printing film hardness so as to achieve the present invention.

General formula (1)



(In the formula, D⁺ stands for a positive ion pigment that has an absorption in a near infrared area; R₁, R₂, R₃ and R₄ separately stand for an alkyl group, an aryl group, an alkyl group, an allyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alicyclic group and a saturated or unsaturated heterocyclic group; at least one of said Rs is said alkyl group of 1 to 8 carbon atoms.)

More specifically, the present invention is a near infrared photocuring ink characterized in that said ink demonstrates a sensitivity on a 700 or more nm near infrared light due to the fact that said near infrared photopolymerization initiator as indicated by general formula (1) is contained in an ethylene unsaturated group containing monomer and an ethylene unsaturated group containing prepolymer that are usually used as activated vehicles for a printing ink.

Said monomer and said prepolymer refer to a monomer that contains one or more ethylene unsaturated groups, for example, a monomer that contains a vinyl group or an allyl group and a prepolymer that contains ethylene unsaturated groups on the end or the side chain. As for the examples, the following types of ethylene unsaturated substances are given: bisphenol A or phenol novolac epoxy resin; epoxy resin of epoxidized soybean oil, epoxidized rosin or epoxidized polybutadiene; epoxy acrylates as substances obtained after acrylic acid and methacrylic acid have been reacted to each other; epoxymethacrylates; urethane modified substances of said epoxy acrylates and methacrylates; ethylene unsaturated group containing resin of ester acrylate and methacrylic ester of fatty acid modified alkyd resin; ethylene unsaturated monomers of ester acrylate and methacrylic ester of the following substances: urethane acrylate; urethane methacrylate; epoxy acrylate; epoxy methacrylate; bisphenol A tetraethylene glycol diacrylate; bisphenol A tetraethylene glycol dimethacrylate; bisphenol F polyethylene glycol diacrylate; bisphenol F polyethylene glycol dimethacrylate; tricyclodecan dimethylol dimethacrylate; trimethylol propane tripropoxy triacrylate; trimethylol propane tripropoxy trimethacrylate; ditrimethylol propane tetraacrylate; ditrimethylol propane tetramethacrylate; trimethylol propane polyethoxy triacrylate; trimethylol propane polyethoxy trimethacrylate; hydroxypivalic neopentyl glycol diacrylate; hydroxypivalic neopentyl glycol dimethacrylate; dipentaerythritolpenta (or hexa); acrylate or methacrylate; tripentaerythritol; tetrapentaerythritol.

Among said substances, the following substances can be preferably used: epoxy acrylates and urethane modified substances of epoxidized soybean oil and epoxidized rosin; ester acrylate of fatty acid modified alkyd resin; urethane acrylate; ester acrylate and ester

methacrylate of the following compound: urethane methacrylate; epoxy acrylate; epoxy methacrylate; bisphenol A tetraethylene glycol diacrylate; trimethylol propane tripropoxy triacrylate; tripentaerythritol; tetrapentaerythritol.

A positive ionic dye borate complex as indicated by general formula (1) is used as a near infrared photopolymerization initiator; the following types of pigments that have an absorption in a near infrared area are used as specific types of said positive ion dye: a cyanine pigment; a triarylmethane pigment; an aluminum pigment; a dianmonium pigment; R_1 , R_2 , R_3 and R_4 of negative borate ions separately stand for an alkyl group, an aryl group, an alkaryl group, an allyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alicyclic group and a saturated or unsaturated heterocyclic group; at least one of said R_s is said alkyl group of 1 to 8 carbon atoms.

Examples of initiators particularly useful to the present invention are indicated in Table

1.

Table 1

Initiator numbers	Structure	R	Ar	λ (TMPA)
Please refer to the original description	Please refer to the original description			Please refer to the original description
		n-butyl n-hexyl n-octyl	Phenyl Anisyl Phenyl	
		n-butyl n-hexyl n-octyl	Phenyl Anisyl Phenyl	
		n-butyl n-hexyl n-octyl	Phenyl Anisyl Phenyl	

λ indicates an absorption wave length. Ph indicates a phenyl group. TMPA stands for trimethylol propane trimethacrylate.

The near infrared photocuring ink of the present invention is preferably used with a formation such that a near infrared photopolymerization initiator is mixed into a monomer and a prepolymer that contain an ethylene unsaturated groups as described above preferably at 0.01 to 10% by weight, particularly at 0.1 to 5% by weight. The cured film of the near infrared photocuring ink of the present invention can be improved by adding nonreactive solid resin as needed, such as diallyl phthalate resin, cyclic ketone resin, natural resin modified phenol resin or acrylic resin; the amount of said resin added is preferably at 30% or less in relation to that of the near infrared photocuring ink of the present invention:

The near infrared photocuring ink of the present invention can be combined with the following agents as needed other than a coloring pigment: a polymerization inhibitor; a plasticizer; a filler; a solvent; aides such as an oxygen removing agent and a chain-transfer agent.

Said ink of the present invention is useful for the following printing means that use ultraviolet photocuring inks: a sheet-fed lithography; a metal-plate printing; an off-rotary printing; a business-form printing; a label- sheet printing; a curved-surface printing; an off-letterpress printing; a *tanpo* printing; a screen printing; said ink is also useful as a coating agent for brightening a sheet, a protective coating and a soldering resist.

After said near infrared photocuring ink of the present invention has been printed onto a sheet, a plastic or a metal, said applied ink is cured by radiating a near infrared ray by using a semiconductor laser, a halogen light or a light-emitting diode; by said means, a printed film with an excellent strength can be obtained.

Said ink can be used as a sheet-fed lithography ink; said near infrared photocuring ink is printed at a 5 μm thickness, and a near infrared ray is radiated by using a near infrared ray radiating device; by said means, said ink is fixed at a dry state onto an aluminum foil sheet that does not have a permeability and a drying property.

The present invention is described with reference to the embodiments.

Embodiment 1

The following substances at the following amounts are kneaded together by using three rollers so as to obtain a near infrared photocuring ink A: a 40 part by weight pentaerythritol triacrylate; a 35 part by weight urethane acrylate (U-108-A produced by Shin Nakamura Chemical Corporation); a 5 part by weight bisphenol A tetraethylene glycol ditriacrylate; a 19 part by weight Rubine GL-SE (produced by Nippon Kayaku Corporation); a 1 part by weight near infrared photopolymerization initiator (initiator No.1).

Embodiment 2

The following substances at the following amounts are kneaded together by using three rollers so as to obtain a near infrared photocuring ink B: a 40 part by weight pentaerythritol tetraacrylate; a 30 part by weight epoxyacrylate (*Karayaddo* [Translator's Note: the word is

not located in any dictionary] R-167 produced by Nippon Kayaku Corporation); a 10 part by weight trimethylol propane tripropoxy triacrylate; a 19 part by weight Rubine GL-SE (produced by Nippon Kayaku Corporation); a 1 part by weight near infrared photopolymerization initiator (initiator No.1).

Embodiment 3

The following substances at the following amounts are kneaded together by using three rollers so as to obtain a near infrared photocuring ink C: a 35 part by weight pentaerythritol triacrylate; a 35 part by weight urethane acrylate (U-108-A produced by Shin Nakamura Chemical Corporation); a 5 part by weight bisphenol A tetraethylene glycol ditriacrylate; a 19 part by weight Navy Blue 2G-SF 200 (produced by Nippon Kayaku Corporation); a 2 part by weight near infrared photopolymerization initiator (initiator No.4A).

Embodiment 4

The following substances at the following amounts are kneaded together by using three rollers so as to obtain a near infrared photocuring ink D: a 40 part by weight dipentaerythritol pentaacrylate; a 30 part by weight epoxy acrylate (*Karayaddo* R-167 produced by Nippon Kayaku Corporation); a 10 part by weight bisphenol A tetraethylene glycol ditriacrylate; a 19 part by weight Navy Blue 2G-SF 200 (produced by Nippon Kayaku Corporation); a 0.5 part by weight near infrared photopolymerization initiator (initiator No.6A).

Comparative Example 1

A near infrared photocuring ink E is obtained as similarly to as in Embodiment 1 except that the near infrared photopolymerization initiator (initiator No.1) is replaced with a 10 part by weight o-benzoyl benzoic methyl.

Evaluating Method for Ink Performance

Curing period: Embodiment 1 to Embodiment 4 and a 0.6 g ink are developed onto carton sheets by using an R1 tester; light is radiated onto said inks by using an aluminum coat halogen light (2 W/cm^2); after this, said inks are pressed against art sheets by using said R1 tester; the radiating periods (seconds) required until the inks stop adhering are defined as the curing periods.

Film hardness: the inks are applied onto hard vinyl chloride plates by using a bar coater so as to obtain a 10 micron film thickness; a radiation is applied for 1 second by using said aluminum coat halogen light (2 W/cm^2) so as to cure said inks. Following this, a pencil hardness is measured for each case based on a JIS-K-5400.

The measuring results of said curing periods and said pencil hardness are indicated in Table 2.

Table 2

Ink	Curing period (second)	Pencil hardness
A	0.5	5H
B	0.5	5H
C	0.5	5H
D	0.5	5H
E	Uncured	-

(6) Advantageous Result of the Invention

The present invention offers a near infrared photocuring ink with a high curing speed and a high film hardness that cures with a near infrared ray.

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